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CHARACTERISTICS OF BIODIESEL AS A FUEL FOR DIESEL ENGINES

Boban Nikolić[1], Breda Kegl[2], Saša Milanović[1], Nikola Petrović[1], Saša Marković[1]

[1]University of Niš, Faculty of Mechanical Engineering in Niš, Serbia

[2]University of Maribor, Faculty of Mechanical Engineering in Maribor, Slovenia

Abstract. *In order for an alternative liquid fuel to be applied to diesel engine operation, it must have certain advantages or must not have major disadvantages compared to conventional diesel fuel. Based on numerous research and practical experiences, it can be said that the use of biodiesel and mixtures of biodiesel with diesel fuel, in this sense, gives the best results. The main advantages of using biodiesel in comparison to fossil diesel fuel can be seen from a strategic, economic and environmental aspects. Producing biodiesel from different raw materials and different technological biodiesel production processes can result in different individual physical and chemical characteristics of fuel. For biodiesel usage as a fuel in diesel engines, it is necessary that the processes taking place in fuel delivery systems, injection processes, mixture formation and combustion of biodiesel, as well as emission characteristics, are fully studied and clear. But above all, it is very important that the characteristics of biodiesel (and mixtures) comply with the appropriate standards. Also, the influence of characteristics that are not prescribed by the standards (sound speed, Bulk modulus, surface tension, etc.) but are very important from the aspect of influence on injection processes, mixture formation, combustion and exhaust gas emissions, must be investigated in detail. The paper provides an analysis of certain characteristics of biodiesel and their possible influences on the biodiesel quality and diesel engines operation when biodiesel is used as fuel.*

Key words: *Diesel engine, Fuel, Biodiesel, Sound Speed, Density, Bulk Modulus*

1. INTRODUCTION

Piston engines with internal combustion are by far the most important power unit of locomotion vehicles, which originates from their favorable properties - low specific mass (kg/kW), i.e. high specific power (kW/kg), compactness (small value of engine capacity

*Received: January 27, 2024 / Accepted February 05, 2024.
Corresponding author: Boban Nikolić
University of Niš, Faculty of Mechanical Engineering in Niš, Serbia
E-mail: boban.nikolic@masfak.ni.ac.rs

per power m^3/kW), quick readiness for work (even in cold conditions), controllability, durability, etc., as well as the fact that they use fuel with a high energy potential (kJ/kg). High concentration of energy in naphtha (oil) and relatively easy work with it, made oil derivatives the basic fuels of IC engines.

With the development of industry and transport, oil, as a universal fuel, has long since gained strategic importance at the global level.

The desire to control the exploitation and distribution of fossil fuels has been causing geopolitical crises since the beginning of mass application, and it seems that this is manifested with even greater intensity in the twenty-first century.

On the other hand, the total human activity on Earth has significantly disturbed the ecological balance. The mentioned situation regarding classical energy sources, its historical and futuristic dimension, the dependence of most countries on the import of crude or refined oil, the resulting financial, political and military crises, as well as the strengthening of environmental awareness, have led to an intensive examination of existing oil reserves, but also an intensification of research in the field of obtaining and applying alternative energy sources.

Special attention is focused on the possibility of obtaining and applying liquid alternative fuels as IC engines fuel. As potential alternative fuels for diesel engines or raw materials for its production, this applies in particular to vegetable oils. Considering that vegetable oils are renewable sources, they represent a potential safe source of energy in the long term.

The main drawback of pure vegetable oil, which prevents its use in classic diesel engines with direct injection, is the molecular structure of this oil - excesivelly large molecules that cause high kinematic viscosity and high surface tension. Comparative characteristics of diesel fuel and some vegetable oils are given in Table 1.

Table 1 Comparative characteristics of diesel fuel and some vegetable oils

Property	Unit	Diesel[a)]	Pure vegetable oil from:			
			Rapeseed[b)]	Soya	Sunflower	Palm
Molar mass	g/mol	120 - 320[d)]	~ 900[d)]	~ 900[d)]	~ 900[d)]	-
Density at 15 °C	kg/m^3	820 - 845	900-930, ~914[c)]	~918[c)]	~917[c)]	~910[c)]
Viscosity at 20 °C	mm^2/s	3 - 8[d)]	~78[d)], ~81[c)]	~78[c)]	~76[c)]	~96[c)]
40 °C		2 - 4.5	max 36	~29[d)]	~30[d)]	-
Flash point	°C	min 56	min 220, ~246[e)]	~254[e)]	~274[e)]	~330[e)]
Iodine value	mgJ/100g	-	95-125, 94-102[f)]	137-143[f)]	119-135[f)]	51.5-57[f)]
Cetane number	-	min 51, ~51.7[c)]	min 39, ~38[c)]	~38[c)]	~37[c)]	~42[c)]
Lower heating value	MJ/kg	~42.5[d)], ~43.1[c)]	min 36, ~39.7[c)]	~39.6[c)]	~39.6[c)]	~36.5[c)]

[a)] EN 590, with FAME max 7% vol., [b)] DIN EN 51605, [c)] [1], [d)] [2], [e)] [3], [f)] [4].

Research conducted with the use of pure vegetable oil in conventional diesel engines with direct injection [2, 5, 6] showed that after about 50 hours of operation, the engine stops working because of large coke deposits on the engine pistons, valves, and especially on the injectors.

Attempts to adapt vegetable oils to the engine are the subject of research in which various substances and additives are added to vegetable oils to obtain fuel with better characteristics and thereby contribute to better performance of the fuel injection system and generally better engine operation.

The best results were achieved by chemical changes of vegetable oils in the direction of reducing molecules (which is one of the main problems with vegetable oils) through esterification with alcohol (ethanol or methanol). By catalytic decomposition of the structure of vegetable oils with alcohol (most often ethanol or methanol), the so-called by oil esterification, it is possible to obtain fuels with completely different characteristics compared to base oils, with a name prefixed with ethyl or methyl ester (e.g. rapeseed oil methyl ester) - commercially known as biodiesel.

By similar chemical processes, biodiesel can also be obtained from waste, already used and processed edible oil, as well as from the remains of animal fats.

2. Biofuels classification

There are many raw materials from which biodiesel can be obtained [5]. Based on their production technologies and development sustainability including all of the implemented influences and effects from cultivation to even after exploitation, biodiesels, like all biofuels in general, can be classified generationally, as shown in Table 2. Producing biodiesel from different raw materials and different technological biodiesel production processes can result in different individual physical and chemical characteristics of fuel. The chemical procedure of esterification of vegetable oil with the aim of producing biodiesel is basically added up to breaking down large and complex molecules into simpler, and in size smaller ones, as previously noted.

Table 2 Generational classification of biofuels [7-10]

Biofuel generation	Raw materials	Processing procedure	Fuel examples
First	sugarcane, oil and other crops also used for food, animal fats	fermentation, esterification	bioalcohols, vegetable oil, biodiesel, biosyngas, biogas
Second	crops not used for food, wheat, corn and similar vegetation, wood, waste	fermentation, esterification, gasification, pyrolysis, etc., thermochemical processes	bioalcohols, vegetable oil, biodiesel, bio-DMF, biohydrogen, bio-Fischer-Tropsch diesel
Third	fast-growing crops and crops cultivated on “barren soil”, microorganisms, algae, crops developed by molecular biology techniques	same as with the 2nd generation, molecular biology techniques	bioalcohols, vegetable oil, biogas, biohydrogen, biodiesel
Fourth	same as with the 3rd generation and crops developed by genetic engineering	same as with the 3rd generation, genetic engineering, all with the CCS effect	same as with the 3rd generation, all within the BECS concept

The first generation of biofuels (conventional biofuels) is usually made from a raw material base used for food, too.

The second generation of biofuels is produced from crops that are not primarily used for food.

The third generation of biofuels encompasses biofuels obtained from fast-growing crops and crops cultivated on the soil that is not otherwise used for the cultivation of crops used for food, algae, microorganisms, and other crops and organisms developed by molecular biology techniques.

The fourth generation of biofuels also includes genetic engineering in the development and processing procedures of raw materials, which enables the "Carbon Capture and Storage" (CCS) of hydrogen compounds that are formed at the levels of raw materials cultivation (algae and microorganisms) and processing technologies (and would otherwise be emitted into the atmosphere) and their geological storage (e.g. in exploited gas and oil fields) or mineral storage (as carbonates). The bioenergy obtained from the fourth generation biofuels is said to satisfy the "Bioenergy with Carbon Storage" (BECS) concept.

3. Biodiesel properties

General requirements for biodiesel as fuel for diesel engines relate to quality, availability, renewable raw materials for production, appropriate prices and fulfillment of environmental requirements. The quality of biodiesel can be assessed through the compliance of biodiesel characteristics with the prescribed standards and the possibility that biodiesel has advantages or does not have major disadvantages compared to conventional diesel fuel.

The characteristics of biodiesel, to be used as fuel for diesel engines, are defined by standards (ASTM D 6751 in USA, EN 14214 in EU etc.). The current standard in the Republic of Serbia is SRPS EN 14214, which is identical to the corresponding one in the EU (Table 3).

Some comparative characteristics of diesel fuels and certain biodiesels obtained from various basic oils are shown in Table 4, based on [5, 10] where the authors included and summarized numerous studies on different types and characteristics of biodiesel used in research.

3.1 Molar mass and kinematic viscosity

According to [11], the chemical formula of rapeseed oil methyl ester (MER) is $C_{21}H_{38}O_2$ with its molar mass of 323.4 g/mol, while, for example, according to [2] the chemical formula of MER is $C_{19}H_{35.2}O_2$ with its molar mass of around 296 g/mol, which is the consequence of the difference in the basic oil and in the process of esterification itself. It is precisely due to the importance of the degree of esterification that this value is prescribed by a standard – according to EN 14214 (Table 3) the degree of esterification should be at least 96.5%.

The kinematic viscosity of biodiesel is, for the examples from Table 4, in the range from 3.7 to 5.8 mm^2/s and is slightly higher compared to diesel fuel (2 do 4.5 mm^2/s) but it is significantly smaller than for basic oil (Table 1), which is directly related to the degree of esterification. However, for some Palm, Jatropha and Karanja biodiesels (Table

4), higher kinematic viscosity values than those standardized by EN 14214 (Table 3) were observed.

Table 3 Biodiesel standard EN 14214 [5]

Property	Unit	Test method	Limits min	Limits max
Density at 15 °C	kg/m^3	EN ISO 3675 EN ISO 12185	860	900
Viscosity at 40 °C	mm^2/s	EN ISO 3104	3.5	5.0
FAME content	% (m/m)	EN 14103	96.5	
Flash point	°C	EN ISO 2719 EN ISO 3679	101	
CFPP – Cold Filter Plugging Point [a)]	°C	EN 116		+5 summer -15 (-20) winter
Sulfur content	mg/kg	EN ISO 20846 EN ISO 20884 EN ISO 13023		10
Cetane number		EN ISO 5165	51	
Sulfated ash content	% (m/m)	ISO 3987		0.02
Water content	mg/kg	EN ISO12937		500
Total contamination	mg/kg	EN 12662		24
Copper strip corrosion (3h at 50 °C)	Rating	EN ISO 2160	class 1	
Acid value	mg KOH/g	EN 14104		0.5
Linolen. acid methyl ester	% (m/m)	EN 14103		12
Polyunsaturated methyl esters (≥ 4 double bonds)	% (m/m)	EN 15779		1
Group I metals (Na + K)	mg/kg	EN 14108 EN 14109 EN 14538		5
Group II metals (Ca + Mg)	mg/kg	EN 14538		5
Methanol content	% (m/m)	EN 14110		0.2
Monoglyceride content Diglyceride content Triglyceride content	% (m/m)	EN 14105		0.7 0.2 0.2
Free glycerol	% (m/m)	EN 14105 EN 14106		0.02
Total glycerol	% (m/m)	EN 14105		0.25
Phosphorus content	mg/kg	EN 14107 FprEN 16294		4
Iodine value	mg Iodine /100g	EN 14111 EN 16300		120
Oxidation stability (at 110 °C)	h	EN 14112 EN 15751	8.0	

[a)] Climate dependent requirements

This can affect the fuel delivery system operation, fuel injection process, injection fuel jet formation, mixture formation and biodiesel combustion, as well as emission characteristics.

Table 4 Some comparative characteristics of certain biodiesels and diesel fuel [5, 10]

Property	Diesel [a)]	Biodiesel from oil of:						
		Rapeseed	Soya	Sunflower	Palm	Jatropha	Karanja	Algae
Density (15 °C) (kg/m^3)	820-845	869-902	876-925	850-884	859-883	865-882	~894	820-890
Viscosity (40 °C) (mm^2/s)	2-4.5	4.4-5.65	4.1-4.9	4.03-4.98	3.7-5.7	4.84-5.56	4.41-5.8	3.68-4.52
Flash point (°C)	min 56	166-179	171-195	89-187	167-176	170-191	114-168	>160
Cetane number	min 51	> 51-54	48-51.3	~49	59-64.6	51-52	50.8-54.5	51-65.5
Lower heating value (MJ/kg)	~42.5[b)]	36.3-38.2	36.7-38.4	36-38.4	36.3-37.5	38.5	35.9-37.9	33.3-36.5
Cold Filter Plugging Point CFPP (°C)	max +5 summer max -15 winter	-10 to -6	-7 to -2	-4 to -12	10 to14	~2	~3	-2.6 to -11.7
Cloud Point CP (°C)	max +3 summer max -5 winter	-3 to 8	0 to 1	-1 to 4	6 to 16	4-13	6-13.6	~ -5
Iodine value (mgJ/100g)	-	97.4-114	120-133	~132	50-59	~105	~83	65-109
Oxidation stability (110 °C) (h)	min 20	~6.5	~7.1	0.8-2.7	~14.7	~2.3	~2.98	5.6-95.7

[a)] EN 590, [b)] [2, 11]

3.2 Cetane number and flash point

The minimum value of the cetane number, for both fuels, is prescribed by the corresponding standards as min 51. The higher the cetane number, the easier the ignition and the better the fuel combustion, which can affect the increase in engine power and the reduction of consumption. Furthermore, an increase in the degree of esterification causes an increase in the cetane number [2, 6]. For some biodiesels from Soya and Sunflower (Table 4), a slightly lower cetane number than standardized by EN 14214 was recorded. This should not be a problem because the addition of certain additives can increase the biodiesel cetane number, if necessary.

Flash point as a parameter does not refer to the ignition point in the engine, but rather the temperature at which vapors that can be ignited are released from the fuel. According to the EN 590 standard for diesel fuel it must be above 55 °C, while the minimum value for biodiesel is 101 °C (according to EN 14214). This information is important for fire-safety during storage, distribution, etc. Biodiesels from Table 4 meet this requirement, except for certain Sunflower biodiesels.

3.3 Oxidation stability and iodine value

It is important for fuel (especially for biofuels) that it does not form oxides (precipitate) in contact with air at high temperatures, so the standards define either the maximum amount of the same (less is better) or the minimum time (most often in the number of hours) for which the fuel shows the corresponding oxidation stability (higher is better). In terms of oxidation stability, biodiesel from palm and algae oil (for the largest number of species) show excellent results (Table 4). Biodiesels from Rapeseed and Soybeans can be said to be at an acceptable level, while Sunflower, Jatropha and Karanja biodiesels more often have problems with oxidation stability (Table 4) and this should be kept in mind.

The iodine value is an indicator of stability of biodiesel against oxidation. A biodiesel with a higher iodine value oxidizes more easily in contact with air and shows a greater tendency to polymerize and form residue in injectors and piston rings. The iodine value depends on the raw material from which biodiesel is produced and it is limited by various standards in different parts of the world – in the EU (EN 14214 – Table 3) and Japan it is maximally up to 120 (in the EU even up to 130 for biodiesel as fuel-oil), up to 140 in South Africa, not limited in Brazil, while in the USA, Australia and India it is not even included in the standards (so as not to exclude the raw materials such as Soybean and Sunflower oil from the production of biodiesel - for which two the values from Table 4 exceed the limit value according to EN 14214) [5, 10].

3.4 Cloud Point and Cold Filter Plugging Point

As diesel fuel contains paraffins, at low temperatures their crystals firstly begin to separate, and the temperature at which the first crystals appear is called the Cloud Point (CP).

When the fuel starts to become cloudy due to the low temperature, it can still reach the engine. When the temperature is so low that the fuel can no longer pass through the fuel filter, we speak of the Cold Filter Plugging Point (CFPP). According to the EN 14214 standard, this temperature is +5 °C for summer or -15(-20) °C for winter biodiesel. Researchers often do not specify for which season (summer or winter) the biodiesels they use are for, but based on the researchers' region of origin, it can be concluded that CFPP and CP values are mostly within the required limits for biodiesels from Table 4, except for Palm oil biodiesel where CFPP values should be corrected with appropriate additives, and it is recommended to pay attention to this parameter for Jatropha and Karanja biodiesels.

3.5 Fuel density

Fuel density is a multiple important parameter. If we look at it through the amount of energy per volume unit of fuel, it would be important that the density of the fuel is as high as possible. However, fuels with a higher density than prescribed can cause problems in the fuel supply system operation, and have a negative impact on the fuel injection process, the quality of fuel atomization, the fuel spray formation, air-fuel mixtures, etc. [5]. Fuels with a lower density than prescribed by the standards can also cause problems in the fuel supply system operation. At the same time, it should be considered that diesel engines are set according to the characteristics of diesel fuel as a reference fuel. Also, the density is in direct connection with the fuel pressure wave speed in the fuel supply system and the fuel Bulk modulus [12]. The biodiesel injection characteristics can be improved by adding different additives [5, 13], for example, ethanol [14].

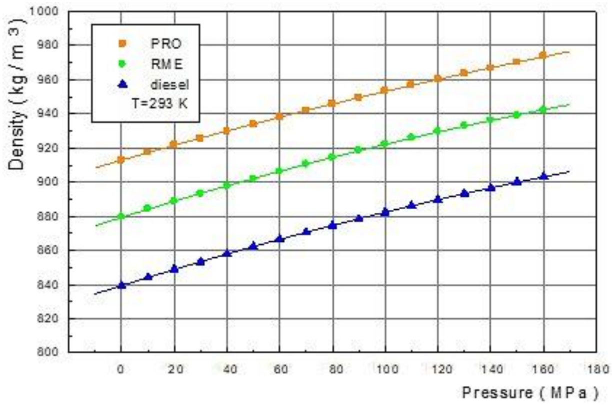

Fig. 1 Density for tested fuels. Experimental values. [5, 12, 15]

Limit values of biodiesel density according to EN 14214 (Table 3) are 860 - 900 kg/m^3 (at 15 °C and atmospheric pressure). These are slightly higher values compared to the diesel fuel values according to EN 590, at 15 °C and atmospheric pressure (Table 4), but in the fuel injection system operation at higher pressures (and temperatures), the density values of biodiesel and diesel differ significantly from the valuesprescribed by the standards. Experimental research [5, 12, 15] has clearly shown this tendency (Fig. 1) and it should be considered from the design phase to the analysis of the fuel injection system operation, especially when the operating pressures are high, which is the case with modern fuel injection systems.

3.6 Fuel lower heating value and oxygen content

The values of the fuel lower heating value (for both diesel and biodiesel) are not prescribed by the standards, as well as the values of the oxygen content in the both fuels compositions, the fuel pressure wave speed (i.e., speed of sound), Bulk modulus and surface tension. These fuel characteristics can be very influential on the fuel supply system operation, fuel injection, etc., and finally on engine performance and exhaust emissions.

The lower heating value of biodiesel is lower than the lower heating value of diesel fuel by approx. 10-15% and even up to 22% - for some Algae biodiesel (Table 4). The consequences can be lower values of effective power and torque, more significant at higher engine speeds (5–10%), with an increase in effective specific fuel consumption by about 12% [16].

As a significant biodiesel characteristic, the oxygen mass ratio (oxygen content) is at around 10% [17], i.e., 11–15% [18]. The presence of oxygen in the biodiesel composition is important from the perspective of combustion and partially compensates for the impact of the slightly lower heating value of biodiesel compared to diesel fuel.

3.7 Sound speed, Bulk modulus and surface tension

The values of sound speed, Bulk modulus and surface tension of biodiesel (and diesel fuel) are not prescribed by the standards but are very important for the fuel injection system operation, the injected fuel spray formation, combustion and exhaust emission quality. These values are different for biodiesel compared to diesel fuel. It is important to note that the values of sound speed and Bulk modulus depend on the operating pressure (Figs. 2 and 3) and temperature [5, 12, 15]. For a diesel engine that is set to work with diesel fuel, this can be the cause of different fuel injection system operating parameters and beyond.

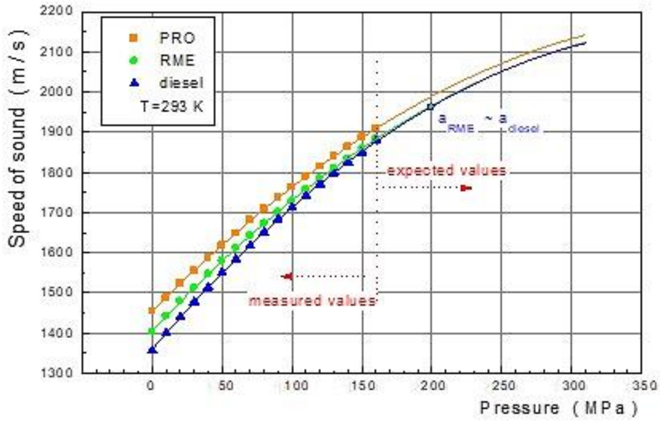

Fig. 2 Speed of sound for tested fuels
(PRO – pure rapeseed oil; RME – rapeseed biodiesel)
Experimen. values from atm. to 160 MPa and expected values for higher pressures [5, 15]

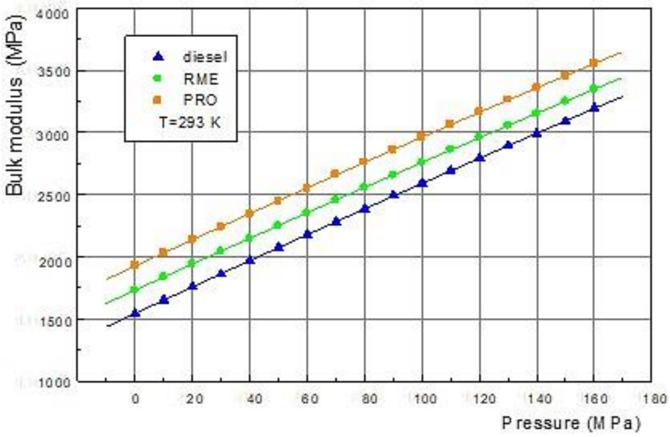

Fig. 3 Bulk modulus for tested fuels calculated by
experimental values of speed of sound and density [5, 15]

4. THE INFLUENCE OF FUEL CHARACTERISTICS ON THE FUEL INJECTION SYSTEM OPERATION

The different values of Bulk modulus, density and speed of sound (as well as viscosity and surface tension) of biodiesel (B100) compared to diesel fuel (and B50 blends of 50% biodiesel and 50% diesel) have impact on the operation of the fuel injection system.

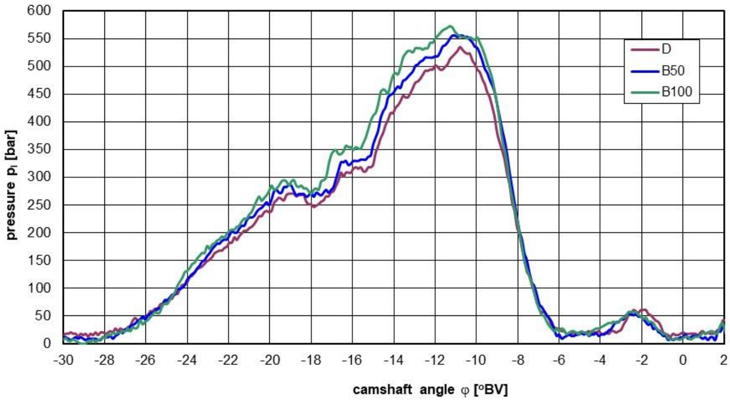

Fig. 4 Fuel influence on the pressure behind the high-pressure pump p_I [5]

The maximum pressure of p_I (pressure behind the high-pressure pump) is slightly higher when using B100 than that of diesel (Fig. 4) [5].

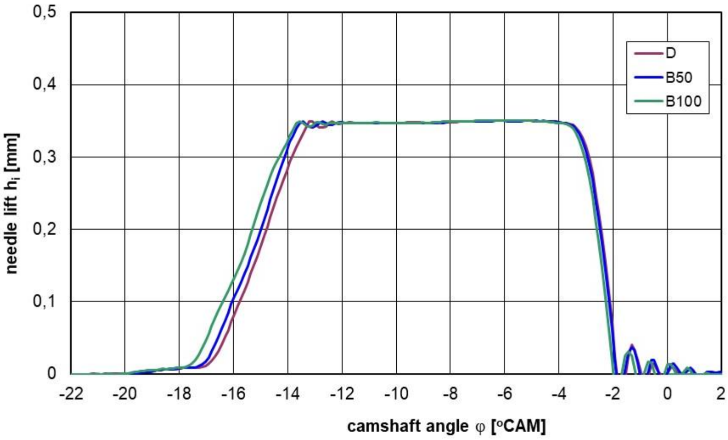

Fig. 5 Fuel influence on needle lift h_n [5]

Biodiesel maximum injection pressure p_{II} (fuel pressure before the fuel injector) is higher compared to diesel fuel (Fig. 6) [5]. In the shown example, the values by type of fuel are: $p_{II\ max\ B100}$ = 590 bar, $p_{II\ max\ B50}$ = 562 bar i $p_{II\ max\ D}$ = 534 bar (Fig. 7). The larger differences are at higher loads.

The higher p_{II} pressure and the density value as well as the advanced start of needle lift results in longer injection duration which raises the amount of injected biodiesel per cycle compared to diesel (differences range up to 7%). The values for B50 are between the values for B100 and D (Fig. 8).

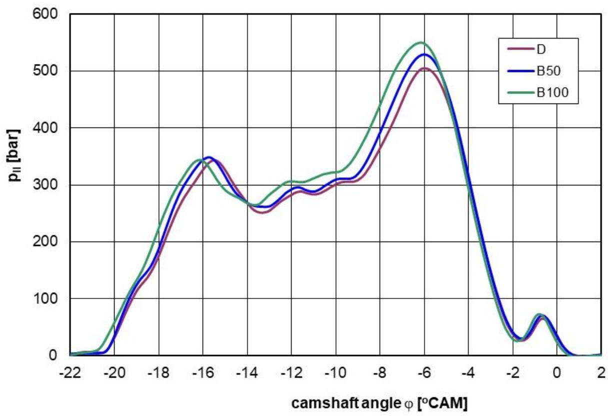

Fig. 6 Fuel influence on pressure p_{II}, camshaft speed 1000 min^{-1} [5]

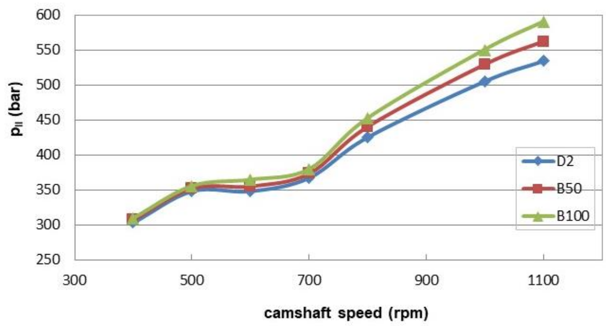

Fig. 7 Fuel and camshaft speed influence on maximum pressure p_{II} values [5]

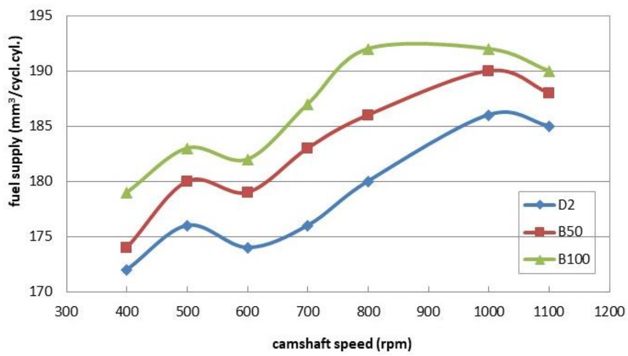

Fig. 8 Fuel and camshaft speed influence on cyclical fuel supply [5]

5. CONCLUSION

Regardless of the type of raw material base for obtaining biodiesel, pure/crude oil is not suitable for direct use as a fuel for modern diesel engines. The base oil, most often of vegetable origin, must be adapted to the numerous requirements of the diesel engine.

The best results were achieved by esterification of vegetable oils to reduce the molecules. By catalytic degradation of the structure of vegetable oils with alcohol, esters of base oils (biodiesel) are obtained, with characteristics close to those of diesel fuel.

Due to the very different possible raw material base and different technological production processes, biodiesels can have different values of certain characteristics, standardized or non-standardized. This can lead to wrong conclusions about biodiesel as a diesel engine fuel, especially if biodiesel with characteristics deviating from the standard limits is used in tests as a diesel engine fuel.

It is necessary to align the biodiesel (and mixtures) characteristics with the appropriate standards and that there is a stable source of biodiesel with constant properties.

Also, it is important that processes that take place in the fuel supply systems, injection and mixture formation processes, as well as knowledge of biodiesel characteristics that are not prescribed by standards (speed of sound, bulk modulus, surface stress, etc.), are fully studied and clear.

Research shows that the use of different biodiesel, with standard characteristics, has an impact on the mentioned processes.

Regarding the differences in the fuel injection system operation, when using biodiesel compared to diesel fuel, it has been observed that there occur a slightly higher maximum fuel pressure behind the high-pressure pump, an earlier start of the injector needle lift, and a higher fuel injection pressure, which, together with the higher value of biodiesel density, result in a longer injection duration and an increased amount of biodiesel injected per cycle.

In order for the operation of a diesel engine with biodiesel to be as similar as possible to the operation of an engine on diesel fuel, or even better, it is necessary to implement the knowledge about the variable values (depending on pressure and temperature) of standardized and non-standardized characteristics of both fuels, as well as the possibility of automatic engine operation setting by previously "identifying" which fuel or which mixture of biodiesel and diesel the engine uses.

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